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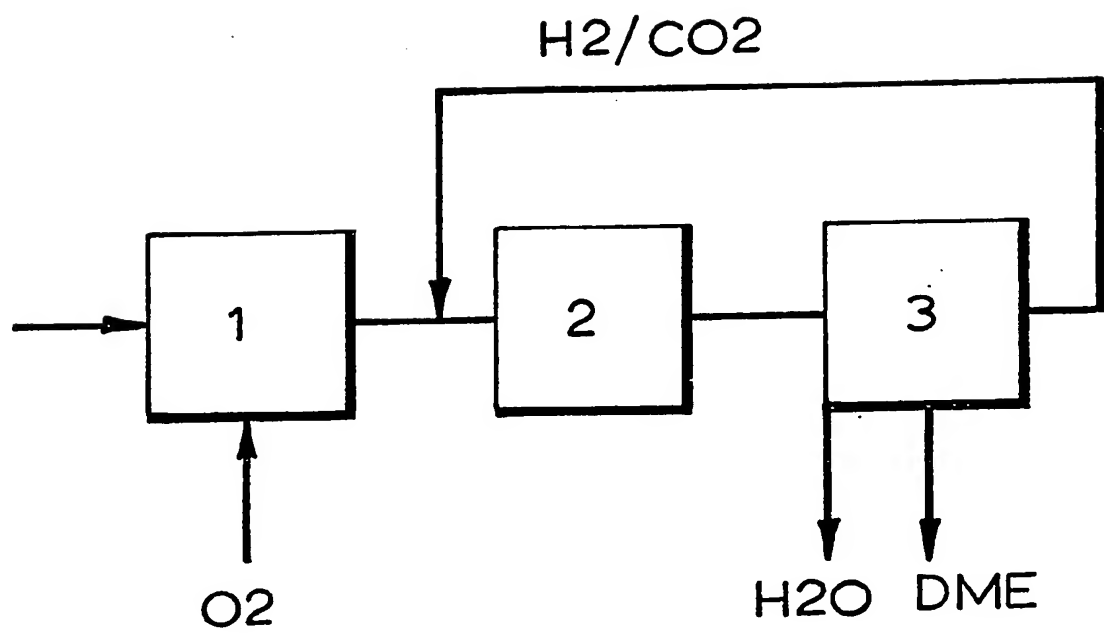
(54) Production of dimethyl ether

(57) The invention relates to a process for the production of dimethyl ether by feeding synthesis gas in a reactor with a catalyst composition and withdrawing a dimethyl ether-containing effluent wherein carbon dioxide obtained from the reactor effluent is recycled to the reactor.

Preferably synthesis gas containing 1.5 - 2.5 moles of hydrogen per mole of carbon monoxide is fed into a reactor containing a catalyst composition comprising a methanol synthesis catalyst and a dehydration catalyst and dimethyl ether and water are separated from the effluent stream. The reaction proceeds under such conditions that substantially only water and no carbon dioxide is rejected.

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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PROCESS FOR THE PRODUCTION OF DIMETHYL ETHER

The invention relates to a process for the production of dimethyl ether (DME) by reacting a gaseous mixture comprising hydrogen and carbon monoxide (syngas) in the presence of a catalyst composition.

5 Dimethyl ether is a valuable product as an energy carrier and a useful starting material for further chemical processes, especially as an intermediate for the conversion into light olefins and/or gasoline. For the production of these desired hydrocarbon products dimethyl ether is as acceptable as methanol,
10 however, dimethyl ether is a better energy carrier than methanol and the production of DME has a number of advantages when compared with the production of methanol.

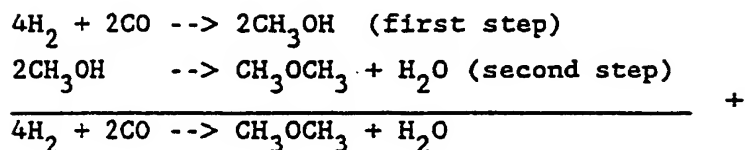
15 First of all the equilibrium conversion of syngas into DME is much higher than that of methanol synthesis, furthermore the H_2 to CO usage ratio in the production of DME can be lower than for methanol synthesis.

20 Therefore there is a need for an economically attractive industrial bulk manufacturing process, using cheap starting materials, especially syngas prepared from natural gas and operating under attractive economical, environmental and safe conditions, i.e. using rather simple equipment and resulting in a significant reduction of the dimethyl ether cost price. Therefore considerable research and development efforts have been made for a further improved dimethyl ether manufacturing process.

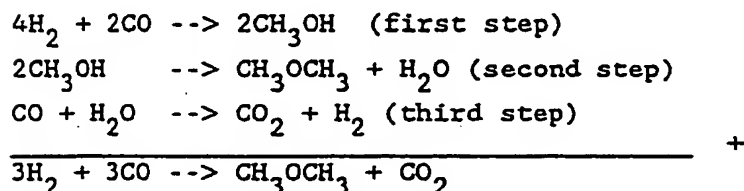
25 It is known that the preparation of DME from a gaseous mixture comprising hydrogen and carbon monoxide can be carried out in two stages as well as in a single stage process.

30 In the two-stage preparation syngas is converted in the first step into methanol by contacting syngas with a methanol synthesis catalyst under suitable conditions and subsequently methanol formed is converted into dimethyl ether by contacting with a dehydration

catalyst under suitable conditions. The reactions progress along the following equations:



5 In the single stage preparation of dimethyl ether syngas is converted by contacting under suitable conditions with a mixture of a methanol synthesis catalyst and a dehydration catalyst under suitable conditions. The reaction can proceed according to the following equations:



10 The one-stage process is generally preferred for reasons set out above. It should be borne in mind that the reactions set out above are in fact equilibria and that special steps must be taken to obtain economically acceptable yields of dimethyl ether.

15 Single-stage processes for the production of dimethyl ether by reacting a gaseous mixture comprising hydrogen and carbon monoxide in the presence of a catalyst composition have been disclosed in the prior art. DME so obtained can be converted into light olefins by known techniques involving a zeolite-type catalyst. Processing DME without separating it from carbon dioxide co-produced may be an advantage if high selectivity to light olefins is aimed at.

20 The single-stage conversion of a gaseous mixture comprising hydrogen and carbon monoxide into dimethyl ether in the presence of a combination of a dehydrating catalyst such as gamma alumina and a methanol synthesis catalyst comprising Cu, Zn and/or Cr and/or Al is known from a number of patent specifications:

DE-A-2757788 discloses the preparation of dimethyl ether from a gaseous mixture comprising CO, H₂ and optionally CO₂ in the presence of a catalyst containing salts or oxides from Al, Cr, La, Mn, Cu, Zn and mixtures thereof which catalyst had been stabilized, with a silicon compound.

GB-A-2093365 discloses the preparation of dimethyl ether from syngas having a H₂/CO ratio of 0.4 - 3 and water in an amount sufficient to compensate for any hydrogen deficiency in the syngas at a temperature of 250 - 400 °C with a catalyst composition comprising Cu, Zn and Al components in certain ratios and a dehydrating component.

GB-A-2097382 discloses a process for the conversion of syngas into dimethyl ether by contacting synthesis gas (H₂/CO ratio of 0.5 - 3.0), optionally together with water and/or an inert gas in the presence of a catalyst comprising co-precipitated Cr, Cu and Zn components in certain ratios and an acidic dehydrating component and subsequently regenerating the catalyst composition by contacting it with an oxygen-containing gas.

US-A-4098809 discloses a process for the production of dimethyl ether from a mixture consisting of CO, CO₂ and H₂, in which the quantity of CO is in substantial stoichiometric excess necessary for methanol synthesis. This proceeds by first forming methanol and then dehydrating the methanol to dimethyl ether. The use of CO rich syngas having low carbon dioxide percentages is advocated because CO and H₂O are converted into CO₂ and H₂ under the prevailing conditions in the reactor and this takes any undesirable H₂O formed by methanol dehydration away, which water would otherwise limit further dehydration of methanol.

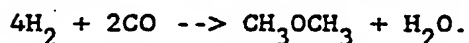
US-A-4011275 discloses the conversion of syngas having a H₂/CO ratio of 0.8 to 1.7 over a conventional two-component dimethyl ether catalyst and states that adding carbon dioxide to the feed had no apparent effect on the dimethyl ether/methanol synthesis.

As the reaction equations given above for the single-stage process show the reaction can proceed under CO₂ rejection, which is unfavourable as to carbon containing starting materials.

An object of the present invention is the development of an industrial process for dimethyl ether manufacture with satisfactory conversion percentages which proceeds without overall CO₂ rejection.

5 The present invention therefore provides a process for the production of dimethyl ether by feeding synthesis gas to a reactor with a catalyst composition and withdrawing a dimethyl ether-containing effluent in which carbon dioxide obtained from the reactor effluent is recirculated to the dimethyl ether reactor.
10 Carbon dioxide is not a simple diluent in the reaction sequence, but may undergo a watergas shift reaction ($\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$) to produce carbon monoxide which is subsequently converted to organic product.

15 The overall reaction taking place according to the present invention can be represented by the following equation:



The process according to the present invention is preferably carried out continuously but can be carried out semi-continuously. Short interruptions of the process to replenish or refresh the catalyst or to purge otherwise accumulating inert gas contaminants
20 may be desirable.

The invention thus substantially prevents the rejection of carbon dioxide during the production of dimethyl ether.

25 The synthesis gas employed in the practice of this invention is preferably hydrogen-rich synthesis gas as can be obtained from natural gas rich in methane by well-known techniques such as catalytic partial oxidation and steam reforming optionally together with carbon dioxide. Syngas which is obtainable by these techniques may contain up to about three molecules of hydrogen per mole of carbon monoxide ($\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2$).
30

The catalysts which can be employed in the practice of the present invention may be made up of mixtures of Group IB, IIB and/or VI metal oxides in combination with a dehydration catalyst.

35 In a preferred embodiment of the invention the process is so carried out that synthesis gas is fed into a reactor containing a catalyst composition, that dimethyl ether and water are separated

from the effluent stream, and that the carbon dioxide containing gaseous fraction of the effluent stream is recirculated to the reactor.

5 The present invention therefore permits the preparation of dimethyl ether from synthesis gas in such a way that overall substantially no CO_2 is rejected by the reaction, but that instead substantially only H_2O is rejected.

10 In a further embodiment of the invention the feed gas to the dimethyl ether reactor contains carbon monoxide and hydrogen in a molar ratio $\text{CO} : \text{H}_2 = 3 : 1$ to $1 : 6$, preferably between $2 : 1$ and $1 : 5$ and the molar ratio $\text{CO} : \text{CO}_2$ between $4 : 1$ and $1 : 3$, preferably between $3 : 1$ and $1 : 1$.

15 The effluent of the dimethyl ether reactor substantially contains dimethyl ether, water, carbon dioxide, as well as any unconverted carbon monoxide and hydrogen starting materials. In accordance with the present invention water is rejected and carbon dioxide and any unconverted carbon monoxide and hydrogen starting materials are recycled optionally after removing contaminants. Preferably the removal of dimethyl ether from the reactor effluent
20 is effected by condensation and phase separation. Subjecting the reactor effluent to cooling or compression, thereby effecting condensation followed by phase separation of the liquid fraction is conveniently effected in a heat exchanger connected to a gas/liquid separator. The gaseous phase from which dimethyl ether and water
25 have been removed can then be recycled, preferably after removal, e.g. by purging of compounds like nitrogen, methane, etc. and supplementing carbon monoxide and hydrogen.

In a further embodiment of the present invention the reaction conditions are so adjusted that the conversion of carbon monoxide
30 into dimethyl ether per pass through the reactor is at least 50%, preferably at least 70%. Favourable reaction conditions employed are within the temperature range of 40 to 540 °C, preferably between 175 and 300 °C and the pressure within the range from 0.5 to 35 MPa, preferably 2 to 10 MPa and a GHSV from 100 to 10,000 N
35 litres of gas per litre of catalyst composition per hour, preferably from 20 to 5,000 N litres of gas per litre of catalyst

composition per hour. The exact reactions employed also depend on the nature of the catalyst used, more in particular its activity.

Catalysts which are preferably used according to the present invention may comprise a methanol synthesis catalyst in combination
5 with a dehydration catalyst. More preferably the methanol synthesis catalyst employed comprises the elements copper, zinc and/or chromium, optionally promoted with another element. Promoter elements are e.g. manganese, vanadium and/or lanthanum. The dehydration catalyst employed preferably may comprise gamma-
10 alumina, silica-alumina and/or a crystalline zeolite.

The dimethyl ether reactor used in the practice of this invention is usually a pipe reactor filled with catalyst in a fixed bed or in a fluidized bed, which reactor may contain one or more heat exchangers which can be cooled with syngas feed to the
15 reactor.

The dimethyl ether synthesis can be carried out in a single reactor or in a series of interconnected reactors. Catalyst material should be of suitable form and size. For fluidized bed technique grinding and sieving prior to use may be necessary. A
20 particle size below 0.4 millimetre is then generally suitable. Also resistance of the catalyst composition towards attrition is important.

A particular favourable manufacturing unit for the practice of this invention is represented by the attached flowsheet. This
25 features a catalytic partial oxidation unit (1) for natural gas to yield syngas, a dimethyl ether reactor (2), a heat exchanger and gas/liquid separator (3) yielding the liquids CH_3OCH_3 and H_2O as well as a gaseous phase mainly comprising H_2/CO_2 , which gas is recycled to the dimethyl ether reactor (2).

30 When the process according to the present invention is operated it is possible by selecting suitable reaction conditions and an active catalyst to prepare dimethyl ether in good yields. In particular, a fresh syngas feed having a ratio of $\text{H}_2 : \text{CO} =$
1.8 : 1, a recycle gas having a ratio of $\text{H}_2 : \text{CO}_2 = 2.2 : 0.6$, and
35 a total feed to reactor with a ratio of $\text{H}_2 : \text{CO} : \text{CO}_2 = 4 : 1 : 0.5$ are suitable. A reaction temperature of about 300 °C, a reactor

5 pressure of about 6 MPa and a reduced Cu-ZnO-Cr₂O₃-catalyst (atomic ratio of the metals 25 : 48 : 27) on gamma-alumina can result in a high once-through conversion. As compounds like nitrogen and methane may accumulate in the recycle stream it is desirable to purge a certain percentage of the recycle gas. Thus it is possible to obtain a once-through degree of conversion of more than 70% using the equipment outlined above. A dimethyl ether purity of over 98% can be obtained.

C L A I M S

1. A process for the production of dimethyl ether by feeding synthesis gas in a reactor with a catalyst composition and withdrawing a dimethyl ether-containing effluent, characterized in that carbon dioxide obtained from the reactor effluent is recycled to the reactor.
5
2. A process according to claim 1, characterized in that synthesis gas containing 1.5 - 2.5 moles of hydrogen per mole of carbon monoxide is fed into a reactor containing a catalyst composition, that dimethyl ether and water are separated from the effluent stream, and that the carbon dioxide-containing gaseous
10 fraction of the effluent stream is recycled to the reactor.
3. A process according to any of the preceding claims, characterized in that the reaction proceeds under such conditions that substantially only water is rejected from the process.
- 15 4. A process according to any of the preceding claims, characterized in that the combined synthesis gas feed and gaseous recycle stream contains carbon monoxide and hydrogen in a molar ratio $\text{CO} : \text{H}_2 = 3 : 1$ to $1 : 6$, preferably between $2 : 1$ and $1 : 5$ and the molar ratio $\text{CO} : \text{CO}_2$ between $4 : 1$ and $1 : 3$, preferably
20 between $3 : 1$ and $1 : 1$.
5. A process according to any of the preceding claims, characterized in that the removal of dimethyl ether from the reactor effluent is effected by condensation and phase separation.
6. A process according to any of the preceding claims,
25 characterized in that the conversion of carbon monoxide into dimethyl ether per pass through the reactor is at least 50%, preferably at least 70%.
7. A process according to any of the preceding claims, characterized in that the catalyst composition in the reactor
30 comprises a methanol synthesis catalyst in combination with a dehydration catalyst.

8. A process according to claim 7, characterized in that the methanol synthesis catalyst comprises the elements copper, zinc and/or chromium and is optionally promoted with another element.
- 5 9. A process according to claim 7 or 8, characterized in that the dehydration catalyst comprises gamma-alumina, silica-alumina and/or a crystalline zeolite.
- 10 10. A process according to any of the preceding claims, characterized in that the operating conditions of the reactor are within the temperature range of 40 to 540 °C, preferably between 175 and 300 °C and the pressure within the range from 0.5 to 35 MPa, preferably 2 to 10 MPa and a GHSV from 100 to 10,000 N litres of gas per litre of catalyst composition per hour, preferably from 20 to 5,000 N litres of gas per litre of catalyst composition per hour.
- 15 11. A process essentially as described hereinbefore with particular reference to the flowsheet.

C10/T1401PD

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Patents Act 1977
Examiner's report to the Comptroller under
Section 17 (The Search Report)

Application number

9105210.0

Relevant Technical fields

(i) UK Cl (Edition K) C2C (CYD, CJM)

(ii) Int Cl (Edition 5) C07C 41/09 43/04

Databases (see over)

(i) UK Patent Office

(ii)
ONLINE DATABASE: WPI

Search Examiner

S I AHMAD

Date of Search

20.2.92

Documents considered relevant following a search in respect of claims

1-11

Category (see over)	Identity of document and relevant passages	Relevant to claim(s)
	NONE	

SF2(p)

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Category	Identity of document and relevant passages	Relevant to claim(s)

Categories of documents

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